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AN APPLICATION OF THE THEORY OF MATERIALS WITH VARIABLE BONDING--ETC(U)
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AN APPLICATION OF THE THEORY OF MATERIALS WITH VARIABLE BONDING TO SOLID PROPELLANT

MICHAEL H. QUINLAN

JUNE 1979

FINAL REPORT
FOR PERIOD 9 NOVEMBER 1976 - 15 APRIL 1979

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AIR FORCE ROCKET PROPULSION LABORATORY
DIRECTOR OF SCIENCE AND TECHNOLOGY
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FOREWORD

This Technical Report was prepared by the Mechanical Behavior and Aging Section (MKPB) of the Air Force Rocket Propulsion Laboratory under Job Order No. 2307M1KT. The principal author was Michael H. Quinlan, now at the University College Cork, Cork City, Ireland. Some sections of the report (as detailed in the Background Section) were written by Durwood I. Thrasher.

This report has been reviewed by the Information Office/XOJ and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations. This report is unclassified and suitable for general public release.

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TO ALL RECIPIENTS OF
AFRPL-TR-78-37

ERRATA

On Page 17, the line following Equation (5,3) is incorrect. This line should be corrected to read as follows:

"whenever $c = (\dot{\phi}\ (1-\alpha) + \alpha\mu) \ / \ \alpha\mu = 0$, and"

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The development of a constitutive theory for materials with variable bonding (materials which respond to applied deformations by rupture of particle-to-particle bonds) is described. The theory is applied to materials in which bond breakage can be represented as a rate process. The result is a constitutive law which represents the stress response to an applied strain as the sum of a linear viscoelastic stress component and a stress component due to 'bonding' (bond breakage). The bonding stress component is linearly related to the bonding rate; the bonding state is governed by a nonlinear ordinary differential

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equation.

The constitutive law was applied to data from tests on TP-H1011 propellant. (The tests utilized cyclic loading of the propellant to provide a mixture of damaged and undamaged propellant responses.) The overall rms difference between calculated and measured propellant response was 2.7 psi over a measured stress range of -3.6 psi to 73.7 psi. The agreement was much closer for the damaged propellant response than for the undamaged (or virgin) propellant response.

The results are judged to be sufficiently promising to justify further effort based on the theory.

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1.0 BACKGROUND

This report is the interim product of more than eight years of research by Dr. Michael Quinlan. He was sponsored and provided with facilities by the AFRPL during the period October 1975 through October 1977 as a National Research Council Postdoctoral Research Associate. From October 1977 through April 1979, Dr. Quinlan continued work on the theoretical development and analysis of propellant test data (generated during his work at the AFRPL) at University College Cork, Ireland.

Equipment and propellant samples, and some technical support for Dr. Quinlan's experimental efforts, were provided under AFRPL In-House Project 573013NE, Solid Propellant Mechanical Behavior. Subsequent support was provided under AFRPL Project 2307M1KT, Propellant Constitutive Theory, until Dr. Quinlan returned to Ireland in 1977. His work since that time was conducted without support from the Air Force by mutual agreement.

Dr. Quinlan authored Section 3, Theoretical Development. Section 3 comprises the major content of this report. The remainder of the report was authored by the current Air Force Project Manager, Durwood Thrasher.

2.0 EXPERIMENTATION

Varied experiments were performed by Dr. Quinlan during his research at the AFRPL on two propellants: ANB-3066 (a carboxy-terminated polybutadiene (CTPB) propellant containing ammonium perchlorate and aluminum) and TP-H1011 (a polybutadiene–acrylic acid-acrylonitrile (PBAN) propellant containing ammonium perchlorate and aluminum).

Much of the testing was done to gain qualitative results on the general mechanical behavior of the two solid propellants as well as to develop a characterization technique to allow determination of a specific nonlinear constitutive law.

The test specimen used is portrayed in Figure 1(a). The specimen is a cylindrical uniaxial tensile bar, carefully milled to achieve a uniform diameter. The ends of the specimen were cut using a razor blade and a special jig to obtain square ends and a reproducible length. The ends of the specimen were bonded to aluminum end tabs using epoxy adhesive. A jig was used to assure accurate alignment. The aluminum end tabs were designed to fit into special grips and incorporated set screws to clamp the end tabs securely. This feature prevented slipping of the specimen in the grips under load reversal. Considerable effort was expended to eliminate play and lost motion in the load linkage of the test machine. Some troublesome "strange" propellant behavior was, in fact, traced to elastic "play" in a part of the load linkage.

The testing was performed using a standard laboratory tensile tester, manufactured by Instron Corporation. The test assembly included a gas dilatometer manufactured by Dr. Richard J. Farris, and the dilatometer load cell was used to measure force on the specimen. The specimen extension was determined from crosshead travel of the tensile tester. A temperature conditioning unit was used to maintain a stable "room temperature" 77°F

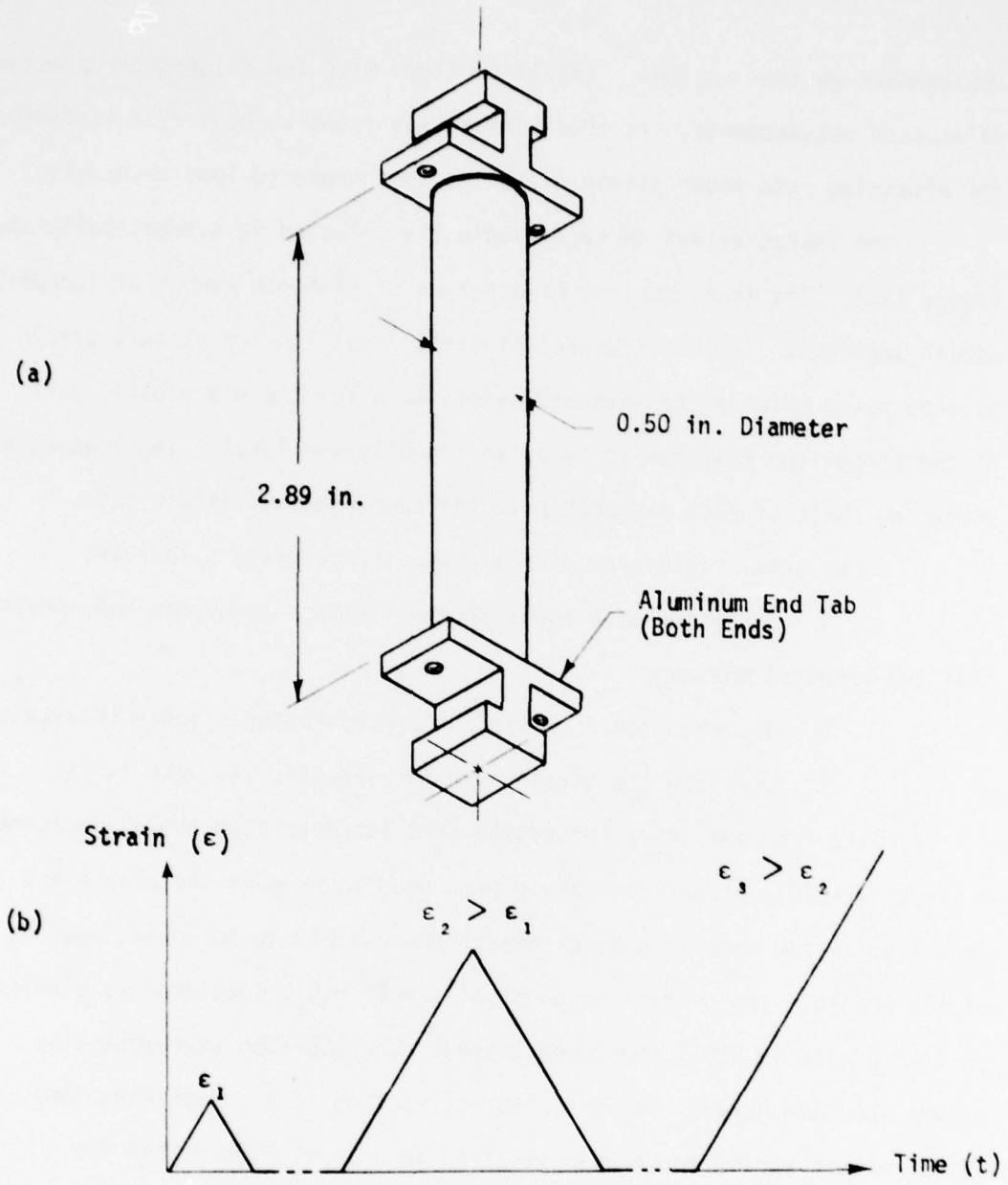

Figure 1. Propellant Testing Approach. (a) Specimen Configuration; (b) Schematic Strain History

environment on the specimen. (While problems with the dilatometer precluded dilatation measurements, its load linkage was found to be very satisfactory for obtaining data under strain histories that produced load reversals.)

The characterization test eventually selected is schematically shown in Figure 1(b). The test consists of a series of sawtooth events of increasing strain amplitude. A long (several minutes) "rest" period at zero strain is interposed between the sawtooth events to allow the visoelastic part of the propellant response to decay to a negligible level. The loading and unloading parts of each sawtooth have the same constant strain rate.

Some useful variations of the above strain history include:

a. Insertion of a sawtooth event with a lower maximum strain than the previous maximum.

b. Insertion of a relaxation process between sawtooth events.

c. Changing the strain rate for specific sawtooth events.

Data from the characterization test (as described above) performed on a single TP-H1011 propellant sample were used to produce the propellant constitutive law constants described at the end of the following section of the report. The overall response of the TP-H1011 specimen was similar to that of all TP-H1011 specimens tested. The ANB-3066 specimens also showed the same general response characteristics (e.g., rejoining the virgin stress-strain curve when strained to a level higher than the previous maximum strain). These characteristics have, of course, been widely observed and reported for solid propellants in general.

3.0 DEVELOPMENT AND APPLICATION OF THEORY

3.1 Introduction

We consider the behavior of cylindrical solid propellant bodies, of small diameter-to-height ratio and weight, subject to small deformations which preserve, and are parallel to, the axis. A temporal sequence of deformations emanating from the same equilibrium state at time zero and terminating at some individual current time is called a process and the average traction subsiding on the disk boundaries upon termination is called the force-response. The value of a deformation in a process at a given time is the axis length at that time divided by its initial length. Assuming that the force-response to any given process is unique, our task is, then, to adequately describe, or model, this correspondence.

Structurally, propellants consist of minute (i.e., in the order of microns) rigid particles densely embedded in a rubbery-like polymer. Such materials respond to processes with an alteration in the amount of species to species bonding - hence the idea of a process inducing or creating a particular current state of bonding. An adequate continuum description of bonding changes can be effected by the introduction of an equivalance relation on the totality of processes. The intuitive interpretation attached to two processes being equivalent is that they both induce the same state of species to species bonding at their respective current times. The validity of taking such a concept as being basic can only be measured by our ability to frame intuitively plausible and useful axioms; useful in the sense of ultimately unravelling the force-response function. Of course if one is persuaded to accept

(6,1) and (6,2) as being basic on the basis of matching experimental data, then all considerations related to bonding can be ignored. This would be as unjustified as to accept the Navier equation of elasticity, with all boundary conditions in terms of displacements, and ignore the concept of stress.

Allied to the notion of a state of bonding is the idea of continuing or extending a process for any preassigned length of time so that the extended and original process create the same state of bonding. As the preassigned lengths of time are allowed to increase without bound, we suppose that the corresponding current stretches tend to a limit. This limit, called a *bonding parameter*, serves to label the state of bonding created by the original process.

The physical requirement that a unique state of bonding subsist in each equilibrium state is equivalent to the requirement that all processes with the same bonding parameter create the *same* state of bonding and conversely. Assuming that such is the case, the set of all processes with the same bonding parameter, and hence each state of bonding, can be *identified* by a unique number, namely, the bonding parameter of any, and hence all, processes in the set. Correspondences of this type are not uncommon in mechanics, indeed, material particles are defined by the requirement that they can be put into one-one correspondence with points in a Euclidean space. Further associations, while important, are entirely subjective.

These ideas suitably axiomatized, serve as a basic framework for acquiring an explicit knowledge of the evolution of bonding states (i.e., the bonding parameter at each time versus time) in a process.

Motivated to some extent by reaction rate theory and the fact that various integral representations are inadequate, we explore the possibility of representing the various evolutions of bonding states as the corresponding solutions of an ordinary differential equation.

3.2 Basic Structure

Let an open neighbourhood D of unity in the strictly positive reals be given. Then a process φ of *duration* $d_\varphi > 0$ is a continuous function

$$\varphi : [0,d_\varphi) \to D \quad ; \quad \varphi(0) = 1$$

whose right derivative ϕ is piecewise continuous. An extension $\varphi(\sigma)$ of a process φ is called a σ- *static continuation* provided that $\varphi^{(\sigma)}(t) = \varphi(d_\varphi)$ for all $t \in (d_\varphi, d_\varphi+\sigma)$ where $d_\varphi+\sigma$ is the duration of $\varphi^{(\sigma)}$! The notation φ_t for $t \in [0,d_\varphi)$ is used to denote the process gotten by restricting φ to $[0,t)$.

A process $\hat{\varphi}$ gotten by extending a process φ such that $\hat{\varphi}_t \sim \varphi$ for[1] all $t \in (d_\varphi, d_{\hat{\varphi}})$ is called a *frozen bonding continuation* of φ. On the question of whether each process can be so-continued, and if so, for how long?, we assert that

AM_2 Each process φ has a *unique* frozen bonding continuation φ^δ of duration $d_\varphi+\delta$ for each $\delta > 0$ and that the limit

$$\pi(\varphi) \stackrel{def}{=} \mathrm{Lim}_{\delta\to\infty}\, \varphi^\delta(d_\varphi+\delta)$$

exists.

We note that AM_2 is a strengthened version of axiom 2 in [1]. The statement that a *unique* state of bonding subsists in a given equilibrium configuration means that the (generally different) frozen bonding continuations of φ and $\hat{\varphi}$ seek the *same* ultimate stretch whenever $\varphi \sim \hat{\varphi}$ and conversely. Mathematically this statement is:

AM_1(b) Let φ and $\hat{\varphi}$ be processes. Then

$$\varphi \sim \hat{\varphi} \quad \text{iff} \quad \pi(\varphi) = \pi(\hat{\varphi}).$$

Clearly, a given state of bonding is induced or created by some process φ and all processes $\hat{\varphi}$ that create the same bonding as φ

[1] $\varphi \sim \hat{\varphi}$ means that φ and $\hat{\varphi}$ create the same state of bonding.

satisfy $\pi(\varphi) = \pi(\hat{\varphi}) = \pi_o$ in which case π_o characterizes the state uniquely. The positive number $\pi(\varphi)$ is called the *bonding parameter* corresponding to the process φ. It follows that axiom 2 part (b) in [1] is an immediate consequence of AM_2 and $AM_1(b)$.

Clearly, the bonding state created by $\varphi^{(\sigma)}$ ought to become constant as σ increases without bound in which case $\varphi^{(\sigma+\delta)}$ is essentially a frozen bonding continuation of $\varphi^{(\sigma)}$ for all σ sufficiently large and each $\delta > 0$.

$AM_1(a)$ Let φ be any process. Then

$$\pi(\varphi^{(\sigma)}) \to \varphi(d_\varphi) \text{ smoothly as } \sigma \to \infty.$$

The qualification smoothly is taken to mean that the derivative of $\sigma \mapsto \pi(\varphi^{(\sigma)})$ exists and limits to zero as $\sigma \to \infty$. A knowledge of events prior to time zero is irrelevant iff an equilibrium state subsists at time zero. Let $s(\varphi)$ be the force-response (stress) to the process φ and let the statement that $\hat{\varphi}$ is a *right translation* of the process φ be taken to mean that $\varphi(t) = \hat{\varphi}(t+\delta)$ for all $0 \leq t < d_\varphi$ and $\varphi = 1$ on $(0,\delta)$ and $d_{\hat{\varphi}} = d_\varphi + \delta$ for some $\delta > 0$. Then the assumed existence of an equilibrium state at time zero is entirely equivalent to:

E Let φ be a right translation of the process $\hat{\varphi}$. Then $\varphi \sim \hat{\varphi}$ and $s(\varphi) = s(\hat{\varphi})$.

We note that in [1], E is implicit in the definition of a process class.

Let the processes φ and $\hat{\varphi}$ have identical duration times. Then the (pointwise) difference $\varphi - \hat{\varphi}$ and the distance $d(\varphi,\hat{\varphi}) = \sup\{|\varphi(t)-\hat{\varphi}(t)| : t \in [0,d_\varphi)\}$ are well defined. If, say, $d_{\hat{\varphi}} < d_\varphi$ we form the right translation $\tilde{\varphi}$ of $\hat{\varphi}$ with $d_{\tilde{\varphi}} = d_\varphi$ and take the distance from $\hat{\varphi}$ to φ to be $d(\tilde{\varphi},\varphi)$. Clearly the totality of processes has the structure of a psuedo-metric space with respect to d.

It is a simple matter to recast the theory of materials with variable bonding as presented in [1] with axiom 1 (resp.2) replaced by the weaker (resp. stronger) AM_1(resp.AM_2), and verify that the various definitions, assumptions, and propositions, if not unaltered, have obvious content preserving modifications.

3.3 Bond Breakage and Formation as a Rate Process

The *possibility* of representing bond breakage and formation as a rate process is mathematically equivalent to finding a function P such that the bonding

$$t \in (0,d_\varphi) \to \pi(\varphi_t) \tag{3,1}$$

corresponding to any process φ may be characterized as the *unique* function satisfying

$$\dot{\pi}(\varphi_t) = P(\pi(\varphi_t), \varphi(t), \dot{\varphi}(t)) \quad \forall \quad 0 < t < d_\varphi \tag{3,2}$$

together with the limit condition

$$\pi(\varphi_t) \to 1 \text{ as } t \downarrow 0$$

by virtue of E. We tacitly assume that (3,1) has the smoothness properties of a process on $(0,d_\varphi)$. Clearly, then, (3,1) has a unique continuous extension to $[0,d_\varphi)$ and the notation $\pi(\varphi_0)$ is meaningful. Throughout the remainder of this section we let φ be a generic process.

Subject to an a fortiori verification, we proceed upon the supposition that such a continuous function P exists. Clearly AM_1 part (a) and the continuity of P ensure that $P(\pi(\varphi), \varphi(d_\varphi),0) = 0$. Conversely, suppose that the value of P at $(\pi(\varphi), \varphi(d_\varphi),0)$ is zero, then $\varphi^{(\sigma)}$ and the constant function

$$\pi \in [d_\varphi, d_\varphi+\sigma) \to \pi(\varphi)$$

satisfy (3,2) on $[d_\varphi, d_\varphi+\sigma)$ for each $\sigma > 0$. Since this solution must be unique and AM_1 part (a) must be satisfied, we infer that $\pi(\varphi) = \varphi(d_\varphi)$. Clearly, then, the restriction

$$P(\pi(\varphi), \varphi(d_\varphi), 0) = 0 \quad \text{iff} \quad \pi(\varphi) = \varphi(d_\varphi) \tag{3,3}$$

must always be satisfied.

Since each process must have a frozen bonding continuation, it follows from (3,2) that the algebraic equation

$$P(\pi(\varphi), \varphi(d_\varphi), \cdot) = 0$$

must have at least one root $\rho(\varphi)$. We require that $\rho(\varphi)$, called the neutral rate corresponding to φ, be unique.

For φ to have a unique frozen bonding continuation up to time $d_\varphi+\delta$, it is both necessary and sufficient that a unique function

$t \in [d_\varphi, d_\varphi+\delta) \to z(t)$ exists such that

$$P(\pi(\varphi), z(t), \dot{z}(t)) = 0; \quad z(d_\varphi) = \varphi(d_\varphi); \quad \dot{z}(d_\varphi) = \rho(\varphi) \tag{3,4}$$

for all $t \in [d_\varphi, d_\varphi+\delta)$. While necessary conditions that ensure existence are not currently available, a plausible sufficiency condition, that ensures existence for all sufficiently small $\delta > 0$, is, namely:

$$P(\pi(\varphi), \varphi(d_\varphi), \cdot) \text{ has a non zero derivative at } \rho(\varphi) \tag{3,5}$$

This condition, demanding that the rate of change of bonding be locally directed by the process rate, suffices to establish the existence of an open neighbourhood O of $\varphi(d_\varphi)$ and unique continuously differentiable function

$$C(\pi(\varphi), \cdot) : O \subset D \to R$$

called the *neutral rate function* such that

(a) $C(\pi(\varphi),\ \varphi(d_\varphi)) = \rho(\varphi)$

(b) each forward solution to

$$\dot{z} = C(\pi(\varphi), z) \quad ; \quad z(d_\varphi) = \varphi(d_\varphi) \tag{3,6}$$

satisfies (3,4) uniquely.

We require that (3,5) be satisfied, thereby ensuring that φ has a unique frozen bonding continuation up to $d_\varphi+\delta$ for all δ sufficiently small. It follows that AM_2 is satisfied if (3,6) has a solution on $[t,\infty)$ (cf sec 3.4).

A Taylor series expansion of $P(\pi(\varphi_t),\ \varphi(t),\cdot)$ about $\rho(\varphi_t)$ yields the first order approximation:

$$\dot{\pi}(\varphi_t) = \hat{\alpha}(\pi(\varphi_t),\ \varphi(t))\ [\dot{\varphi}(t)-C(\pi(\varphi_t),\ \varphi(t))] \tag{3,7}$$

In view of (3,3)

$$C(\pi(\varphi_t),\ \varphi(t)) = 0 \text{ iff } \varphi(t) = \pi(\varphi_t). \tag{3,8}$$

We assume that $\hat{\alpha}$ is the constant function with value α.

To avoid a return to the classical theory of viscoelasticity, modulo a driving term Φ (c.f.[1], sec. 9) we assume that $\alpha \neq 1$. Finally in view of

$$\dot{\pi}(\varphi_t) = \alpha\ \dot{\varphi}(t) \text{ when } \pi(\varphi_t) = \varphi(t)$$

we impose the growth conditions $0 < \alpha < 1$.

3.4 Frozen Bonding Continuations; The Neutral Rate Function

Let the processes $\hat{\varphi}$ and φ have the same current bonding parameter π_o and satisfy

$$0 < \eta_o = \hat{\varphi}(d_{\hat{\varphi}}) - \pi_o = (\varphi(d_\varphi) - \pi_o) \tag{4,1}$$

For significant values of η_o, experience of bond reformation (resp. rupture) indicates that each frozen bonding continuation of φ (resp. $\hat{\varphi}$) ought to be weakly increasing (resp. significantly decreasing) in each sufficiently small right neighbourhood of d_φ. This implies that $\rho(\varphi) = C(\pi_o, -\eta_o + \pi_o)$ (resp. $\rho(\hat{\varphi}) = C(\pi_o, \eta_o + \pi_o)$) ought to be small and positive (resp. significantly negative). Clearly, then, the function

$$\eta \to C(\pi_o, \eta + \pi_o) \stackrel{\text{def}}{=} \hat{C}(\pi_o, \eta)$$

is defined in a neighbourhood N of zero and is plausibly of *exponential* character in the sense that:

NRF There exists an upper bound $\mu(\pi_o)$ such that the derivative of $\eta \to c(\pi_o, \eta) - \mu(\pi_o)$ is proportional to itself; the constant of proportionality $\upsilon(\pi_o)$ being strictly positive.

Immediately, then,

$$\hat{C}(\pi_o, \eta) - \mu(\pi_o) = c(\pi_o)\, e^{\upsilon(\pi_o)\eta} \quad \forall \ \eta \in N.$$

As a consequence of (3,8), it follows that $c(\pi_o) = -\mu(\pi_o)$. Moreover if $\upsilon(\pi_o)$, $\mu(\pi_o)$ and $\bar{\upsilon}(\pi_o)$, $\bar{\mu}(\pi_o)$ satisfy NRF, then the corresponding constants are identical. The assumption that $\mu(\cdot)$ and $\upsilon(\cdot)$ are constant functions with values μ and υ yield the representation

$$\hat{C}(\pi_o, \eta) = \mu(1 - e^{\upsilon\eta}) \quad \forall \ \eta \in N$$

Let φ be any process. Then the restriction z to $[d_\varphi, d_\varphi + \delta)$ of the frozen bonding continuation of φ up to $d_\varphi + \delta$ (if it exists) must be the unique function satisfying

$\dot{z} = \hat{C}(\pi(d_\varphi),\ z-\pi(d_\varphi));\quad z(d_\varphi) = \varphi(d_\varphi)$

on $[d_\varphi, d_\varphi+\delta)$ or, equivalently, be such that $\xi = z - \pi(d_\varphi)$ is the unique function satisfying

$$\dot{\xi} = \mu(1-e^{\upsilon\xi});\quad \xi(d_\varphi) = \varphi(d_\varphi)-\pi(d_\varphi) \tag{4,2}$$

on $[d_\varphi, d_\varphi+\delta)$. The smoothness of $\xi \to \mu(1-e^{\upsilon\xi})$ suffices to ensure that any solution to (4,2) on $[d_\varphi, d_\varphi+\delta)$ is necessarily unique.

Let $t \geq d_\varphi$, then some entirely elementary calculations show that the function ξ with definition: $\xi(t) = 0$ if $\xi(d_\varphi) = 0$ and

$$e^{\upsilon\xi(t)} = \{1-e^{-\mu\upsilon(t-d_\varphi)}\ (1-e^{-\upsilon\xi(d_\varphi)})\}^{-1}, \tag{4,3}$$

if $\xi(d_\varphi) \neq 0$, is a solution to (4,2) on $[d_\varphi, \infty)$. Since the first two terms in the denominator are non negative and the remaining term is strictly positive, $\xi(t)$ is well defined. Furthermore when $\xi(d_\varphi) > 0$ (resp. $\xi(d_\varphi) < 0$), the replacement of $e^{-\upsilon\xi(d_\varphi)}$ by unity shows that the denominator is bounded above (resp. below) by unity in which case $\xi(t) \downarrow 0$ (resp. $\uparrow 0$) as $t \to \infty$. The satisfaction of AM_2 is immediate.

3.5 The Evolution of Bonding States

In order to characterize the bonding (3,1) corresponding to each process φ the unique function satisfying (3,2) it is *necessary* for

$$\dot{\pi} = \alpha\{\phi - \mu(1-e^{\upsilon(\varphi-\pi)})\} \tag{5,1}$$

subject to $\pi(0) = 1$, to have a unique solution π on $[0,d_\varphi)$ or equivalently, upon setting $\xi = \varphi - \pi$, for

$$\dot{\xi} = \phi(1-\alpha) - \alpha\mu(e^{\upsilon\xi}-1) \tag{5,2}$$

subject to $\xi(0)=0$, to have a unique solution ξ on $[0,d_\varphi)$.

Let φ be *piecewise linear* and $I = [i,f]$ be any subinterval of $[0,d_\varphi)$ on which φ is linear. Then (5,2) has the solution $\xi(t) = \xi(i)$ on I whenever $\dot{\xi}(i) = 0$. Otherwise (5,2) integrates to yield

$$e^{\upsilon\xi(t)} = \{\alpha\mu\upsilon(t-i) + e^{-\upsilon\xi(i)}\}^{-1} > 0; \quad t \in I \tag{5,3}$$

whenever $c = (\phi(1-\alpha) + \alpha\mu)/\alpha\mu$

$$e^{\upsilon\xi(t)} = c/\{1-e^{-\gamma(t-i)}(1-ce^{-\upsilon\xi(i)})\}; \quad t \in I \tag{5,4}$$

whenever $c \neq 0$, where $\gamma = \alpha\mu\upsilon c$. Clearly (5,4) is equal to (5,3) in the limit as $c \to 0$. Since the first two terms in the denominator in (5,4) are non-negative (resp non-positive) and the remaining term is strictly positive (resp negative) when $c > 0$ (resp $c < 0$),(5,4) is well behaved. Also, when $c > 0$, the bonding ultimately lags behind the corresponding stretch by the amount,

$$\xi^* = \mathrm{Lim}_{t\to\infty}\xi(t) = (\mathrm{Ln}\ c)/\upsilon \tag{5,5}$$

Since the right hand side

$$(t,\xi) \in I \times R \to \phi(t)\,(1-\alpha) + \alpha\mu(e^{\upsilon\xi}-1)$$

is continuous and locally Lipschitz in ξ, we conclude that the solution ξ corresponding to the initial data $\xi(i)$ is, in fact, unique. Iterating this result we have the desired existence and uniqueness of solution to (5,2) for all piecewise linear processes.

Let φ be the continuously differentiable on $I = [i,f]$. Clearly, then, we can construct a sequence of piecewise linear processes ϕ_n such that $\phi_n \to \phi$ uniformly on I. It follows that

$$\phi_n(t)\,(1-\alpha) + \alpha\mu(e^{\upsilon\xi}-1) \to \phi(t)(1-\alpha)+\alpha\mu(e^{\upsilon\xi}-1)$$

uniformly on I x R. Since for each n, the solution ξ to

$$\dot{\xi}_n = \phi_n(t)(1-\alpha) + \alpha\mu(e^{\upsilon\xi}-1); \quad \xi_n(i) = \xi(i)$$

exists and is unique on I, it follows [2; theorem 2.4] that there exists a subsequence $\xi_{n(1)}, \xi_{n(2)}, \ldots$ such that

$$\xi(t) = \lim_{k\to\infty} \xi_{n(k)}(t) \qquad \forall\ t \in I$$

is a solution to (5,2) on I corresponding to the initial data $\xi(i)$. In view of the smoothness of the right hand side, we conclude that ξ is unique. Since processes are continuous and piecewise continuously differentiable, an iteration of the preceeding result suffices to establish that (5,2) has a unique solution corresponding to each process. The characterization of the evolution of bonding states is, then, complete.

Let φ be any process in which case $\varphi^{(\sigma)}$ is constant on $[d_\varphi, t]$ for all $d_\varphi < t < d_\varphi + \sigma$. Let ξ be the corresponding solution to (5,2) on $[d_\varphi, t]$. Since the value of c corresponding to $\phi = 0$ is unity, we have that ξ^* is zero and hence the implication : the bonding corresponding to $\varphi^{(\sigma)}$ ultimately tends to $\varphi(d_\varphi)$ from above when $\xi(i) < 0$ and below when $\xi(i) > 0$. The satisfaction of AM_1 part (a) is, then, immediate.

3.6 The Basic Equations: Reproduction of Experimental Data

We assume that propellants are fading memory materials in the sense of [1;sec 8]. Following [3;sec 4] and [1;sec 9] together with some obvious linearizations, we have

$$s(\varphi_t) = E_\infty[\pi(\varphi_t)-1] + E_s[\varphi(t)-\pi(\varphi_t)] + E_0 \int_0^t G(t-\tau)\dot{\varphi}(\tau)d\tau + A\dot{\pi}(\varphi_t).$$

The rapidity with which a zero stress state is re-established upon unloading requires that $E_\infty = E_s$. While the process to be considered is extremely general it avoids introducing excessive stress relaxations in which case the stress response ought not to be critically affected by the particular choice of $G(\cdot)$. For convenience we choose $G(t) = t^n$ where $-1 < n < 0$. The explicit governing equations are, then,

$$s(\varphi_t) = E_0 \int_0^t (t-\tau)^n \dot{\varphi}(\tau)\, d\tau + B_0 \dot{\pi}(\varphi_t) \qquad (6,1)$$

and

$$\dot{\pi}(\varphi_t) = \alpha[\dot{\varphi}(t)-\mu(1-e^{\upsilon(\varphi(t)-\pi(\varphi_t))}]; \quad \pi(\varphi_0) = 1 \qquad (6,2)$$

Using the testing approach discussed in Section 2.0, a propellant specimen of the configuration shown in Figure 1(a) was subjected to the characterization test described in Section 2.0. The series of increasing amplitude sawtooth events (see Figure 1(b) at a strain rate of 0.0058 inches per second was followed by a sawtooth event terminating at a strain below the previous maximum, then by sawtooth events at both higher and lower rates and to various amplitudes. The actual piecewise linear process is represented in Table 1. Data points were taken from the tensile tester's pen recorder ("strip chart") plots of load cell output versus time. The stretch values (φ (t)) were calculated from the crosshead rate and time (chart distance) values using the known sample length.

TABLE 1

TEST DATA AND CALCULATION RESULTS FOR TP-H1011 PROPELLANT

t(secs) *	φ(t)	π(t)	$\dot{\varphi}$(t)(ins/sec)	Computed s(φ)(P.S.I.)	Measured s(φ)(P.S.I)
0.0	1.000	1.0000	0.0	0.0	0.0
0.70	1.004	1.0002	0.0058	4.47	5.20
1.70	1.010	1.0005	0.0058	7.47	10.50
2.70	1.016	1.0008	0.0058	10.64	16.25
3.70	1.021	1.0013	0.0058	14.64	21.65
4.40	1.025	1.0018	0.0058	18.64	26.00
4.76 (1)	1.027	1.0021	0.0058	21.32	28.15
5.20	1.025	1.0023	-0.0058	12.53	14.30
5.70	1.022	1.0023	-0.0058	9.10	9.40
6.70	1.016	1.0022	-0.0058	4.52	4.75
7.70	1.010	1.0020	-0.0058	1.16	1.60
8.70	1.005	1.0017	-0.0058	-1.73	-0.80
9.52	1.000	1.0015	-0.0058	-3.93	-2.80
11.22	1.000	1.0015	0.0	-1.00	-1.10
16.22	1.000	1.0015	0.0	-0.49	-0.50
23.22	1.000	1.0015	0.0	-0.29	-0.30
803.22	1.000	1.0006	0.0	-0.01	0.0
804.12	1.005	1.0009	0.0058	5.06	5.00
805.12	1.011	1.0012	0.0058	8.03	8.50
806.12	1.017	1.0015	0.0058	11.22	12.50
807.12	1.022	1.0020	0.0058	15.34	17.75
808.12	1.028	1.0028	0.0058	21.80	28.00
809.12	1.034	1.0044	0.0058	32.28	34.50
809.75 (2)	1.038	1.0060	0.0058	40.60	38.35
810.12	1.036	1.0067	-0.0058	25.63	21.75
811.12	1.030	1.0074	-0.0058	13.27	11.00
812.12	1.024	1.0074	-0.0058	7.77	6.65
813.12	1.018	1.0072	-0.0058	4.12	3.85
814.12	1.012	1.0069	-0.0058	1.14	1.50
815.12	1.007	1.0067	-0.0058	-1.57	-0.65
816.28	1.000	1.0063	-0.0058	-4.55	-3.15
818.25	1.000	1.0063	0.0	-1.44	-1.30
835.25	1.000	1.0063	0.0	-0.40	-0.25
1375.25	1.000	1.0041	0.0	-0.04	0.0
1376.15	1.005	1.0044	0.0058	4.99	4.75
1377.15	1.011	1.0047	0.0058	7.87	8.10
1378.15	1.017	1.0050	0.0058	10.77	11.50
1379.15	1.022	1.0053	0.0058	14.13	15.00
1380.15	1.028	1.0059	0.0058	18.85	19.75
1381.15	1.034	1.0069	0.0058	26.60	27.50
1382.15	1.040	1.0089	0.0058	38.47	39.25
1383.00 (3)	1.045	1.0117	0.0058	49.72	45.00

* Symbols in circles identify points of peak strain (See Figure 2).

TABLE 1 (CONT)

TEST DATA AND CALCULATION RESULTS FOR TP-H1011 PROPELLANT

1383.65	1.041	1.0130	-0.0058	25.41	20.50
1384.15	1.038	1.0134	-0.0058	18.76	15.50
1385.15	1.032	1.0135	-0.0058	11.76	9.65
1386.15	1.027	1.0134	-0.0058	7.66	6.40
1388.15	1.015	1.0129	-0.0058	1.68	1.85
1389.15	1.009	1.0126	-0.0058	-0.95	0.0
1390.75	1.000	1.0122	-0.0058	-4.97	-3.20
1392.20	1.000	1.0122	0.0	-1.94	-1.45
1426.20	1.000	1.0120	0.0	-0.33	-0.20
2026.20	1.000	1.0088	0.0	-0.06	0.0
2028.00	1.010	1.0092	0.0058	7.49	7.30
2030.00	1.022	1.0098	0.0058	13.06	13.40
2032.00	1.033	1.0108	0.0058	21.21	22.50
2033.50	1.042	1.0128	0.0058	34.74	34.10
2034.50	1.048	1.0155	0.0058	47.91	47.50
2035.80 (4)	1.055	1.0211	0.0058	61.99	55.60
2036.50	1.051	1.0228	-0.0058	30.70	25.70
2037.50	1.046	1.0234	-0.0058	18.94	15.50
2039.50	1.034	1.0232	-0.0058	9.94	7.70
2041.50	1.022	1.0227	-0.0058	4.20	3.40
2043.50	1.011	1.0221	-0.0058	-0.92	-0.10
2045.39	1.000	1.0216	-0.0058	-5.58	-3.60
2067.07	1.000	1.0215	0.0	-0.69	0.30
2697.07	1.000	1.0176	0.0	-0.08	0.0
2698.57	1.009	1.0180	0.0058	6.61	6.20
2700.57	1.020	1.0185	0.0058	11.88	11.70
2702.57	1.032	1.0191	0.0058	17.23	17.80
2704.57	1.043	1.0201	0.0058	25.52	27.00
2706.07	1.052	1.0222	0.0058	39.54	41.60
2707.07	1.058	1.0251	0.0058	52.72	56.50
2708.47 (5)	1.066	1.0313	0.0058	67.01	65.00
2709.07	1.062	1.0329	-0.0058	37.06	33.20
2710.07	1.057	1.0337	-0.0058	23.70	19.80
2712.07	1.045	1.0335	-0.0058	14.14	10.60
2715.07	1.028	1.0327	-0.0058	5.64	4.20
2717.07	1.016	1.0322	-0.0058	0.60	1.00
2719.87	1.000	1.0314	-0.0058	-6.15	-3.60
2745.22	1.000	1.0312	0.0	-0.81	-0.10
3405.22	1.000	1.0271	0.0	-0.08	0.0
3407.22	1.012	1.0276	0.0058	7.95	7.60
3409.22	1.023	1.0282	0.0058	13.06	12.80
3412.22	1.040	1.0290	0.0058	20.63	21.80
3414.22	1.052	1.0299	0.0058	28.10	31.50
3416.22	1.063	1.0328	0.0058	46.86	54.70
3417.72	1.072	1.0383	0.0058	65.43	70.00
3418.38 (6)	1.076	1.0414	0.0058	71.01	73.70

TABLE 1 (CONT)

TEST DATA AND CALCULATION RESULTS FOR TP-H1011 PROPELLANT

3419.22	1.071	1.0434	-0.0058	36.17	33.80
3420.22	1.065	1.0438	-0.0058	25.75	21.70
3422.22	1.054	1.0436	-0.0058	17.09	12.70
3425.22	1.036	1.0428	-0.0058	8.69	6.00
3428.22	1.019	1.0420	-0.0058	1.18	1.30
3431.54	1.000	1.0410	-0.0058	-6.70	-3.60
3458.29	1.000	1.0409	0.0	-1.00	-0.20
3998.29	1.000	1.0375	0.0	-0.11	0.0
3999.39	1.006	1.0378	0.0058	5.47	4.80
4001.39	1.018	1.0383	0.0058	10.77	10.00
4004.39	1.035	1.0391	0.0058	18.08	17.50
4006.39	1.047	1.0397	0.0058	22.90	23.80
4008.39	1.058	1.0404	0.0058	28.73	33.00
4009.39	1.064	1.0410	0.0058	33.55	39.00
4010.24 (7)	1.069	1.0419	0.0058	40.17	49.50
4010.89	1.065	1.0422	-0.0058	28.22	28.30
4011.89	1.059	1.0423	-0.0058	22.04	19.00
4013.89	1.048	1.0418	-0.0058	14.86	11.00
4016.89	1.031	1.0410	-0.0058	6.63	4.80
4019.89	1.013	1.0402	-0.0058	-0.89	0.20
4022.19	1.000	1.0395	-0.0058	-6.36	-3.60
4048.19	1.000	1.0394	0.0	-0.90	-0.30
4648.19	1.000	1.0356	0.0	-0.11	0.0
4650.19	1.006	1.0359	0.0029	3.90	3.85
4652.19	1.012	1.0361	0.0029	6.47	6.15
4656.19	1.023	1.0367	0.0029	11.19	10.50
4660.19	1.035	1.0372	0.0029	15.70	15.00
4664.19	1.046	1.0378	0.0029	20.22	20.30
4668.19	1.058	1.0387	0.0029	26.07	28.20
4670.19	1.063	1.0398	0.0029	30.88	34.15
4672.09 (8)	1.069	1.0417	0.0029	37.40	44.45
4673.18	1.066	1.0424	-0.0029	28.04	27.75
4675.18	1.060	1.0428	-0.0029	21.79	18.75
4679.18	1.048	1.0425	-0.0029	14.99	11.25
4683.18	1.037	1.0420	-0.0029	9.74	10.50
4687.18	1.025	1.0414	-0.0029	4.91	4.20
4691.18	1.014	1.0408	-0.0029	0.31	1.80
4695.18	1.002	1.0403	-0.0029	-4.16	-1.10
4695.98	1.000	1.0401	-0.0029	-5.03	-2.65
4748.28	1.000	1.0398	0.0	-0.82	-0.30
5318.28	1.000	1.0363	0.0	-0.15	0.0
5318.84	1.007	1.0366	0.0115	7.90	5.85
5319.34	1.012	1.0368	0.0115	10.81	8.80
5320.34	1.024	1.0374	0.0115	16.28	14.40
5321.34	1.035	1.0379	0.0115	21.46	19.95
5322.34	1.047	1.0385	0.0115	26.66	26.50
5323.34	1.058	1.0391	0.0115	33.28	36.50
5323.92 (9)	1.065	1.0397	0.0115	40.50	42.00

TABLE 1 (CONT)

TEST DATA AND CALCULATION RESULTS FOR TP-H1011 PROPELLANT

5324.14		1.063	1.0397	-0.0115	27.30	28.65
5324.59		1.057	1.0396	-0.0115	21.32	19.50
5325.59		1.046	1.0392	-0.0115	13.42	10.50
5326.59		1.034	1.0386	-0.0115	7.34	5.70
5327.59		1.023	1.0381	-0.0115	1.77	2.15
5328.59		1.011	1.0375	-0.0115	-3.58	-1.10
5329.56		1.000	1.0370	-0.0115	-8.60	-4.40
5346.28		1.000	1.0369	0.0	-0.77	-3.00
5796.28		1.000	1.0340	0.0	-0.12	0.0
5801.28		1.006	1.0343	0.0012	3.00	3.20
5811.28		1.017	1.0348	0.0012	7.49	7.15
5821.28		1.029	1.0353	0.0012	11.67	10.90
5831.28		1.040	1.0358	0.0012	15.73	15.00
5841.28		1.052	1.0368	0.0012	20.38	20.40
5845.78	(10)	1.057	1.0378	0.0012	23.22	24.00
5848.78		1.054	1.0382	-0.0012	19.03	17.00
5856.28		1.045	1.0382	-0.0012	14.01	11.00
5866.28		1.033	1.0376	-0.0012	8.97	6.85
5876.28		1.022	1.0371	-0.0012	4.47	3.75
5886.28		1.010	1.0364	-0.0012	0.20	0.95
5895.27		1.000	1.0359	-0.0012	-3.49	-1.75
5970.27		1.000	1.0354	0.0	-0.83	-3.50
6570.27		1.000	1.0317	0.0	-0.17	0.0
6570.72		1.010	1.0322	0.0231	14.44	9.50
6571.22		1.022	1.0327	0.0231	20.38	16.00
6572.22		1.045	1.0338	0.0231	31.82	29.50
6572.72		1.057	1.0344	0.0231	40.07	42.00
6573.27	(11)	1.069	1.0359	0.0231	71.85	63.20
6573.71		1.059	1.0361	-0.0231	21.37	19.00
6574.71		1.036	1.0352	-0.0231	4.35	5.00
6575.71		1.013	1.0341	-0.0231	-7.38	-2.00
6576.26		1.000	1.0335	-0.0231	-13.42	-5.80
6589.76		1.000	1.0334	0.0	-0.66	-2.00
6859.76		1.000	1.0317	0.0	-0.15	0.0
6874.76		1.009	1.0320	0.0006	3.63	3.65
6894.76		1.020	1.0324	0.0006	7.72	7.10
6914.76		1.032	1.0329	0.0006	11.60	10.60
6944.76		1.049	1.0345	0.0006	17.78	17.30
6966.76		1.062	1.0403	0.0006	23.90	25.50
6984.76		1.051	1.0421	-0.0006	15.40	12.90
7014.76		1.034	1.0415	-0.0006	8.32	6.70
7044.76		1.017	1.0405	-0.0006	2.23	2.50
7073.05	(12)	1.000	1.0395	-0.0006	-3.15	-1.50

THE MEAN SQUARE ERROR FOR 179 POINTS IS 2.700

The force-responses

$$t \in [0, d_\varphi) \mapsto s(\varphi_t)$$

in the sixth column (Measured $s(\varphi)$) were calculated from the chart readings using the appropriate factors for calibration and specimen cross-sectional area.

Each trial set of values $\alpha > 0$, $\mu > 0$, $\upsilon > 0$, and $n < 0$ determines corresponding values for ε_0 and β_0 from the requirement that the root mean square error of the force responses as computed from (6,1) and (6,2) minus the corresponding experimentally measured values be a minimum. The Bothm-Powell functional optimization technique [4] established that the values

$$\alpha = e^{-3.05}$$

$$\mu = 0.132 \times 10^{-3}$$

$$\upsilon = 195$$

$$n = -0.103$$

and the corresponding values

$$E_0 = 495$$

$$B_0 = 7679$$

rendered this minimum equal to 2.7 pounds per square inch. Clearly, the tabulated values of $\pi(\varphi_t)$ in Table 1 are entirely compatible with our intuitive expectations (also see the "hysteresis" plots of

$\pi(\varphi_t)$ vs $\varphi(t)$ in Figure 2). In conclusion it must be emphasized that this study is one of an interim nature. The inaccuracies in the force-response reproduction appear traceable to the usage of the power law . This usage was justly criticized by Gurtin in [5].

3.7 Acknowledgements

The development of this theory is primarily due to Dr. R. L. Peeters who initiated the project, served as advisor during the former half of the author's tenure as a National Research Council Post Doctoral Research Associate at the Air Force Rocket Propulsion Laboratory, and carried out the crucial confidence - giving numerical studies on forerunners of the bonding equation. I gratefully acknowledge Mr. Thrasher's service as Project Manager during the latter half of my tenure and his assistance in earlier attempts. I thank the AFRPL for supporting this project, and in particular Dr. R. R. Weiss, for providing the necessary experimental facilities without which a basis "gut feel", and hence the theory as it now stands, would not have developed. A very special thanks goes to Mr. Arch Johnston for experimental assistance. I acknowledge my indebtedness to the authorities of University College Cork, Ireland, for providing the necessary computer facilities and to Mr. L. Touhey for computer facilities. Finally, I thank Prof. M. E. Gurtin for encouragement and vital contributions to the theory.

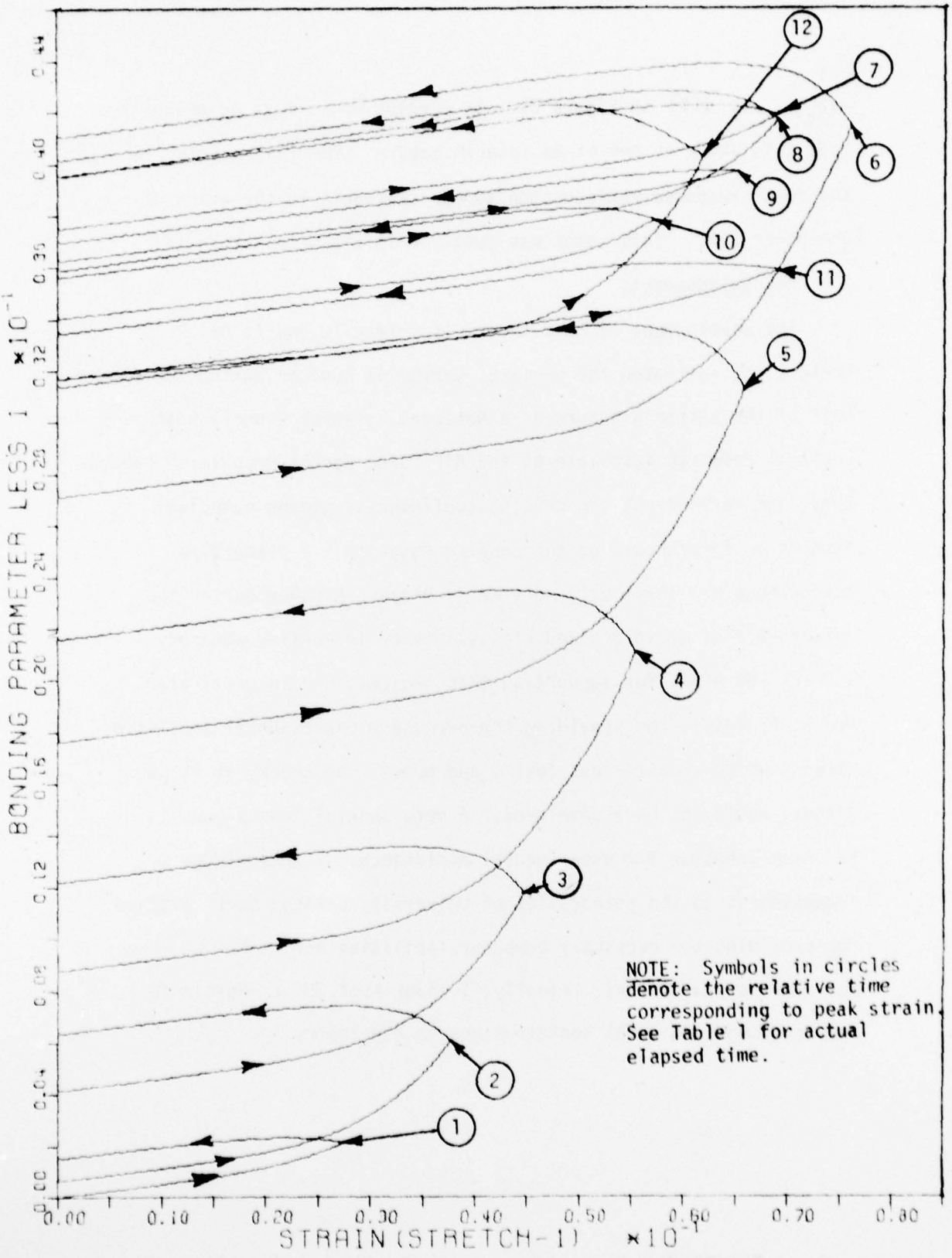

FIGURE 2. STRAIN AND BONDING HISTORY

4.0 CONCLUSIONS

The work represented in this report is considered to be a starting point, with a very firm footing in continuum mechanics, for a usable constitutive theory for solid propellants. As indicated in Section 3.0, the deviation of calculated force-response (or stress) from the measured values is sufficient to be less than totally satisfactory. Dr. Quinlan suspects the power law representation used for the linearly viscoelastic component of the force response as being the cause of this deviation. However, a factor which cannot be ignored is the non-continuous nature of solid propellants, which may require introduction of non-continuum considerations before a totally workable propellant constitutive law can be produced.

The degree to which the results herein reproduce damaged propellant response is extremely encouraging, and further work in this area will undoubtedly resolve the remaining problems.

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APPENDIX - MATHEMATICAL NOTATION

Section 3 of this report uses certain mathematical notation and terminology which may be unfamiliar to many readers of this report. This appendix is intended to aid these readers in following the theoretical development. With the explanations given in this appendix, the remaining development of terminology and use of symbols in Section 3 should be self-explanatory.

The notation used is explained below using a tabular format, in no particular order. Notation which should be clear to most engineers is (hopefully) not included.

NOTATION	MEANING
:	"Such that"; e.g., t:(t-1)=0 means "t such that (t-1) = 0".
ϵ	"Is an element of (a set)"; e.g., a ϵ (A) means "a is an element of the set (A)". Also can be read "belongs to".
$\forall$	"For all".
$\subset$	"Is a subset of"; e.g. C $\subset$ D means " C is a subset of D"
$\rightarrow$	"Approaches"; e.g., a $\rightarrow$ b means "a approaches b".

NOTATION	MEANING
$\downarrow$ or $\uparrow$	"Approaches from above" or "approaches from below"; e.g., $t \downarrow 0$ means the same as "$t \to 0;\ t \geq 0$".
$\to$ or $\mapsto$	"Maps into"; e.g., $f : D_f \to R_f$ means "f such that D_f maps into R_f" where D_f is the domain of the function f and R_f is the range of values assumed by the function. Also, $x \mapsto f(x)$ can be read, "Assign to x (in some obvious domain) a function f(x)"; e.g., $x \mapsto x^2$ is more fully written as $(x)^2$: $(-\infty, \infty) \to [0, \infty]$.
[a,b]	A closed interval, which includes a and b; e.g., $x : [a,b]$ means the same as $x: a \leq x \geq b$.
[a,b)	An interval which includes a but excludes b.
(a,b]	An interval which includes b but excludes a.
(a,b)	An open interval, which excludes a and b.
$(\cdot)$	Means "A variable which is obvious from the context".
$(A,B,\cdot)$	Means the variable represented by $(\cdot)$ is allowed to vary while A and B are held constant.

NOTATION	MEANING
resp.	"Respectively".
sup	Supremum, or least upper bound.
moduluo	"Except for".
Lipschitz	A function which is "Lipschitz" has a continuous derivative. "Locally Lipschitz" is a more stringent restriction than "continuous" and a less stringent restriction than "continuously differentiable".
AM_1, AM_2, NRF	Reference to an axiom (underscored in the statement of the axiom) or an assumption (underscored in the statement of the assumption).
I x R	(As used in the equation following Equation (5, 5) , i.e., $(t, \xi) \in I \times R$) an interval of t (defined previously as a subinterval of $[0, d_\varphi]$) and a corresponding interval of ξ consisting of all real numbers.